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(54) Title: WATER-BORNE FUNCTIONALISED POLYMERS (57) Abstract Water-borne functionalised polymers comprising the addition product of a carbodiimide oligomer and a reactive hydrogen compound and a chain extender, and optionally a polyurethane prepolymer have valuable properties for example as coating and film-forming agents.		

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Water-borne functionalised polymers.

This invention relates to new types of functionalised polymers, to their preparation and to uses based on the effects of the functionalisation on their properties.

Introduction

Various types of polymers are used in the coating and impregnation industries. An important class are the urethane polymers, which generally have advantageous properties such as abrasion resistance, toughness, flexibility, elasticity, and tensile strength. A broad range of properties can be achieved by varying the basic starting materials: isocyanate, hydroxy and/or amine containing materials. Urethane polymers can be prepared in organic solvent systems or in water.

To obtain special additional qualities several types of additives are commercially available, for example crosslinking agents (melamine, aziridine, carbodiimide, and functionalised carbodiimides), hydrophobic compounds (compounds containing a long alkyl chain, or a high level of fluorine atoms) and fire retardants (phosphate esters, antimony derivatives or brominated compounds). All of these additives (except crosslinking agents after crosslinking) can in principle be washed out of the coating system. They further need additional, and sometimes complicated, handling for mixing with the polymer or oligomer system.

This invention provides means by which high molecular weight functionalised resins, preferably having a molecular weight above 20,000 may be produced as dispersions in an aqueous medium which may contain in

addition to water a small quantity, for example at most 10% and preferably at most 5% by weight of organic solvent for example a lower alcohol having 1 to 8 carbon atoms or N-methyl pyrrolidone or dipropylene glycol dimethyl ether based on the total weight of the dispersion. The functionalities are incorporated in the polymer system and confer special properties on the polymer.

Several polyurethane derivatives with special properties have been described. Among them are the self-crosslinkable urethane compounds. A range of UV- curable oligomers have been made by reacting a polyurethane prepolymer with hydroxyethylacrylate, hydroxyethylmethacrylate or castor oil (some recent examples are described in EP 507053; JP 04222883; J. Appl. Polym. Sci 47, (1993), 1089) by the formation of unsaturated groups containing acylurea (US 4328138) by the formation of unsaturated groups containing acylurea end-capped with an unsaturated group (US 5115072) or by the incorporation of glycerin monomethacrylate (J. Appl. Polym. Sci. 1989, 38, 627) or trimethylol propane mono-acrylate (Eur. Polym. J. 1991, 27, 193) in a polyurethane prepolymer. All these types of urethane compounds are oligomeric before the crosslinking takes place and may be prepared in organic solvents. Unsaturated groups can be introduced in polyurethanes by the incorporation of unsaturated polyester diols. The products are cured by addition polymerisation (for example as described in EP 424745), possibly initiated by UV radiation (for example as described in JP 04183770).

A range of alkoxysilane functional polyurethanes

have been described, which crosslink on drying after they have been hydrolysed (Some recent examples are described in Ger. Offen 4002418; US 4542065; and US 4999412).

Hydrophobic groups have been introduced in
5 polyurethanes to obtain water repellency and water resistance. This can be achieved by incorporation of hydroxyfunctional perfluoroalkylpolyethers or polyesters into a polyurethane prepolymer (Some recent examples are described in EP 430266; J. Pol. Sci. Part A: Polym. Chem.
10 1990, 28, 2679) or by incorporation of a perfluoroalkyl-diisocyanate into a polyurethane prepolymer (Some recent examples are described in EP 332405; US 4942164).

Epoxy group containing oligomers can be obtained by capping a polyurethane prepolymer with a hydroxy-
15 functional alkylene epoxide (some recent examples are described in Polym. Int. 31, (1993), 25; JP 04335016).

Tertiary amine functions can be incorporated by the formation of acylurea groups from oligomers which contain carbodiimide groups and tertiary amine containing
20 carboxylic acids (US 4321172).

Several functional groups can be introduced by the reaction of a functional carboxylic acid with a carbodiimide functional oligomer (GB 1569248).

The described methods of introducing additional
25 fuunctionalities in polyurethanes are limited to oligomeric systems, and/or are limited in their application.

In this invention we provide water dispersed polyurethane derivatives which contain functional groups.

It may be desirable for surface coating applications
30 to use polymers of high molecular weight. There is a need in coating compositions to minimise the use of

organic solvents as these are considered to be environmentally harmful and in at least some cases are detrimental to the health of workers exposed to their fumes. The provision of suitable high molecular weight polymers in aqueous dispersions is therefore desirable.

We have developed a new general method of preparing water-borne polyurethanes with side chains which have functional groups. The most important advantages of these products are:

- the functionalities are in the side chains; in general this enhances their effect;
- the products are water-borne, that is, are in aqueous media;
- the products can be non-ionic, anionic, cationic or amphoteric;
- the products can be made polymeric as well as oligomeric;
- polymeric dispersions may be produced which form continuous films when a surface is coated with the dispersions (i.e. are self film forming)
- double bonds may be introduced which renders the resins self crosslinkable under the influence of UV radiation in the presence of photo initiators.

Description of the invention

According to the present invention there is provided a water-borne functionalised polymer comprising:

the addition product of a carbodiimide oligomer and a reactive hydrogen compound HX or HOX, in which X is a polymer modifying group, a chain extender and optionally a polyurethane prepolymer.

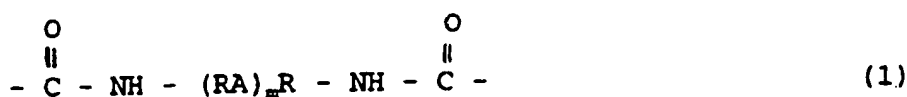
The chain extender is a compound having two

functional groups capable of reacting with two functional groups of the addition product or the oligomer but which does not react with carbodiimide groups in the latter case.

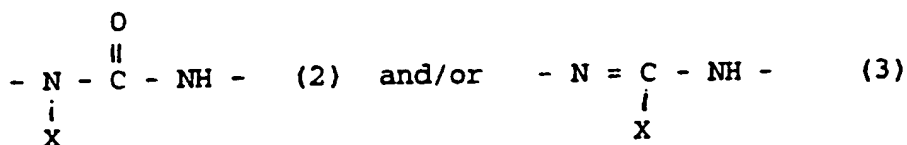
5 It may be a compound of formula $HK (R^{III})_r KH$.

The polyurethane prepolymers may be of formula (7) below.

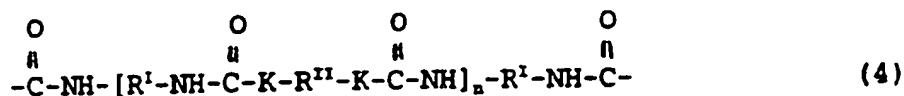
This invention also comprises a water-borne functionalised polymer which comprises repeat units of formula YW and optionally ZV in which p groups of formula YW and q groups of formula ZV are present, in which Y is of formula:



15 in which A is the function resulting from the reaction of a carbodiimide function with a hydrogen active compound HX or HOX and has the formula



20 in which Z is



in which V and W individually have the formula



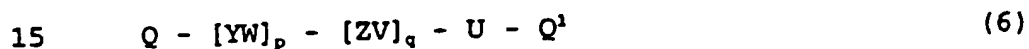
wherein

YW and ZV may be present in any order and may be arranged as randomly or as blocks,

30 R, R^I , R^{II} and R^{III} are independently divalent organic groups which are unreactive towards other functions present in the molecule,

- K and Kⁱ are individually NH or O,
 X is a property modifying group,
 hydrophilic groups are present in R, Rⁱ, Rⁱⁱ, Rⁱⁱⁱ and/or X,
 the ratio of q to p has a value from zero up to twenty
 5 and p is at least one,
 m has a value from one up to twenty,
 n has a value from half up to ten,
 r has a value from 0 to 1 with the proviso that if r=0, K
 is NH, and
 10 p and q and m and n represent statistical mean values and
 thus need not be integers.

The chain length of the polymer of the present invention may be limited to a desired value. The invention also comprises polymers of the formula:



wherein

- Y, Z, W, V are as defined hereinbefore and U is Y or Z,
 Q and Q¹, are individually groups of formula OR^A, NHR^A or
 NR^AB^B and R^A and R^B are individually H, hydrocarbyl or
 20 substituted hydrocarbyl, and p has a value from zero to
 50 and when p is zero U is Y.

- In order to obtain dispersibility in water the group
 Rⁱⁱ or part of the group Rⁱⁱ may contain carboxylic acid,
 sulphonic acid, or sulphuric acid functions or the
 25 corresponding salts, and/or X may contain primary,
 secondary, tertiary or quaternary amine functions, and/or
 part of the groups R, Rⁱ, Rⁱⁱ, Rⁱⁱⁱ or X may contain a
 hydrophilic segment which may be a polyoxyalkylene chain
 which comprises polyoxyethylene units and preferably
 30 consists essentially thereof optionally substituted by a
 sulphonic acid residue.

The property modifying group X is present in an amount of p times m. Since the compounds are polymeric they will contain molecules of different molecular weight and hence the values of p and q may vary in different molecules. For similar reasons the values of n and m in the oligomeric parts Y and Z may vary in different molecules.

The non-capped polymers are self-film forming compounds and the molecular weight preferably will be at least 10,000. The molecular weight of the compound can be adjusted to any desired value depending on the application by capping with Q or Q¹¹ and will then be at least 1000.

Polymers according to the invention may be made by polymerising as a dispersion in an aqueous medium a compound which comprises groups of formula (2) and/or (3) and also two-NCO groups, optionally together with a compound of formula

$$\text{OCN} - (\text{R}^I - \text{NH} - \overset{\text{O}}{\parallel} \text{C} - \text{K} - \text{R}^{II} - \text{K} - \overset{\text{O}}{\parallel} \text{C} - \text{NH})_n - \text{R}^I - \text{NCO},$$

(7) optionally in the presence of a tertiary amine, with a compound of formula $\text{HK} - (\text{R}^{III})_r - \text{KH}.$

The presence of the group X may, depending on the type, confer beneficial properties to the polymer:

- A self-crosslinkable compound may be obtained when X in formula (2) is an unsaturated acyl side chain preferably derived from an unsaturated carboxylic acid having 3 to 20 carbon atoms or when X in formula (3) is an unsaturated amino- or oxy-alkyl side chain preferably having 2 to 20 carbon atoms. The crosslinking can be initiated by radical

initiators and/or by UV radiation.

- A self-crosslinking compound may be obtained when X in formula (3) is an aminoalkyl group substituted with trialkoxysilane functions. The crosslinking takes place by hydrolysis of the alkoxy-silane functions, followed by a condensation reaction in which Si-O-Si bonds are formed.
- Water repellant and waxy-feeling compounds may be obtained when X in formula (2) is an acyl group with a long alkyl chain or when X in formula (3) is an amino- or oxy-alkyl chain with a long chain length.
- Water repellant, oil resistant and stain resistant compounds may be obtained when X in formula (2) is an acyl group with a fluorinated alkyl chain or when X in formula (3) is a fluorinated amino- or oxyalkyl chain.
- Cationic compounds may be obtained when X in formula (2) is an aminoalkyl-acyl chain.
- Hydrophilic compounds may be obtained when X in formula (2) is an alkoxyalkylated acyl chain or when X in formula (3) is an alkoxyalkylated amino- or oxyalkylene group.
- Metal- or amino-crosslinkable products may be obtained when X in formula (2) is acetoacetyl or when X in formula (3) is a methylene diester, a methylene oxyester or a methylene diketone.
- Compounds, which interact with collagen in leather may be obtained when X in formula (2) or (3) contains a functional group reactive to collagen functionality (such collagen functionality is typically a nucleophile such as amine, carboxyl or

hydroxyl). Examples of the functionality in X are carbonyl groups, electrophilically activated olefins and related unsaturated compounds, halogenated aliphatic or aromatic hydrocarbons where the halogen is labile to nucleophiles and phosphonic acid groups.

Other functional groups may also be introduced in X to confer other desirable properties in the polymer. For example groups capable acting as ultraviolet stabilisers, thermal stabilisers, photoinitiators or dyes.

Detailed description of the invention.

The groups R, R^I, R^{II}, R^{III}, R^A and R^B can contain any substituent group which does not significantly interfere in the preparation of the compound and in the chemistry of the final product. Hence the groups R, R^I, R^{II}, R^{III}, R^A and R^B may, for example, include alkyl, ester, or alkoxy side chains or may include a urethane grouping in the main chain. The groups R, R^I, R^{II}, R^{III}, R^A and R^B may be, or include, aromatic groups and the terms "aromatic" and "aryl" are used herein to include fused aromatic rings and also substituted aromatic rings wherein the substituents are non-reactive groups of the type previously discussed herein.

The groups R, R^I, R^{II} and R^{III} are divalent, non-reactive organic groups, and may be divalent hydrocarbon groups which can be alkylene, alkenylene, cycloalkylene, cycloalkenylene or arylene groups or a mixture of these. R, R^I, R^{II} and R^{III} may contain 1 to 30 and preferably 2 to 15 carbon atoms. R, and R^I are typically the hydrocarbon residues of a diisocyanate. R^{III} is typically the

hydrocarbon residue of a diamine, a diol or an amino-alkanol.

R, R^{II} and R^{III} may comprise a hydrophilic segment to improve the dispersibility of the compound in water. The hydrophilic segment is typically a poly(oxy-alkylene) group, preferably a poly(oxyethylene) group, possibly substituted with a sulphonic acid residue. If the hydrophilic segment is present in R, R is the residue of an addition product of two isocyanate containing materials and a poly(oxyalkylene) diol, a poly(oxy-alkylene) diamine, a diol or diamine with a poly(oxy-alkylene) side chain, or a diol or diamine with a poly(oxyalkylene) side chain containing a sulphonic acid residue. In general at least one of the isocyanate containing materials, and typically both is a diisocyanate. The remaining isocyanate functions contribute to the carbodiimide formation, whereafter the carbodiimide functions are further reacted to form the -NX-(C=O)-NH or -N=C(X)-NH- groups.

The hydrophilic segments are generally poly-(oxyalkylene) groups and the number of oxyalkylene groups is preferably sufficient for the group R or R^I and R^{III} to have a molecular weight of at least 100 but preferably not exceeding 10,000. Generally the molecular weight does not exceed 5000, and preferably the molecular weight is between 500 and 2000.

A diamine, diol or aminoalkanol (which gives rise to the group R^{III}) may be used for the chain extension of the polymer. To improve the water dispersibility of the compound the diamine, diol or aminoalkanol may contain alkoxyalkylene functions as described above.

The group R^{II} is suitably a residue of a polyoxy-alkylene diol, for example one of which each alkylene group has 2 to 6 carbon atoms for example polyoxy-ethylene, polyoxypropylene or polyoxybutylene diol, or of polyester diol, for example an aliphatic dicarboxylic acid/alkylene diol chain, an aromatic dicarboxylic acid/alkylene diol chain, a polycaprolactone, a polycarbonate/alkylene diol or a dimeric fatty acid/alkylene diol chain, from which the OH functions have reacted with an isocyanate containing material to form a urethane bond. R^{II} may have a molecular weight of 24 to 5000, preferably from 50 to 3000. To improve the water dispersibility a part of R^{II} can be the residue of an alkanediol with a side chain containing a carboxylic acid, a sulphonic acid or a sulphate.

The end groups $NH-CO-Q$ and $NH-CO-Q^1$ may be derived from a NCO group; for example: $NH-CO-NH-R^A$ and $NH-CO-NR^A R^B$ group may be produced by reaction of the isocyanate group with an alkylamine, a dialkylamine, a hydroxy-alkylamine or a di-(hydroxyalkyl)amine or an $NH-CO-O-R^A$ may be produced by reaction of a isocyanate group with an alkanol. Alkyl or alkylene groups comprised in Q and Q^1 can be saturated or unsaturated and contain 1 to 40 carbon atoms and preferably 2 to 25 carbon atoms. To improve the dispersibility in water the alkyl group can be substituted by a carboxylic acid or it can contain poly(oxyalkylene) functions for example with a molecular weight of 100 to 5000 and preferably 200 to 2000.

X may be introduced by the reaction of a reactive hydrogen containing compound comprising a group X , a group OX , or the corresponding salts, with a carbodiimide

function. When this is a substituted carboxylic acid or salt thereof, the final polymer will comprise the acylurea groups of formula (2), while the reaction with other hydrogen reactive compounds will result in polymers which comprise groups of formula (3). X may preferably contain from 1 to 30 carbon atoms, and typically from 2 to 20 carbon atoms, or may comprise a poly(oxyalkyl) chain with a molecular weight between 100 and 5000 and typically between 200 and 2000.

10 X in formula (2) can be a substituted acyl function. The substituents can be for example, an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkadienyl, alkynyl, or aromatic group; a fluorinated or halogenated alkyl or aryl group; a substituted saturated or unsaturated alkyl, or cycloalkyl group, substituted by for example an amino, 15 an alkylamino, a dialkylamino, an alkoxy, an hydroxy, a thio, an oxo, a heterocyclic, a heteroaromatic, a phosphonic ester, salt of a sulphonic acid, a sulphonic ester, a sulphuric acid or a sulphuric ester group; a 20 poly(oxyalkylated) group.

X in formula (3) can be a primary amine function, a saturated or unsaturated aliphatic amine or an aromatic amine; for example: an alkyl-, cycloalkyl-, alkenyl-, cycloalkenyl-, alkadienyl-, alkynyl-, alkanol-, 25 thioalkyl-, aryl- amine; a poly(oxyalkylated) amine; a substituted alkylamine, substituted for example by an alkylamine, a dialkylamine, an alkoxy, a heterocyclic group, a heteroaromatic group, an alkoxysilane; urea; a thiourea, an alkyl urea; an alkyl thiourea; an hydrazine, 30 an alkylhydrazine, an acetoxhydrazine, a carbethoxyhydrazine, an hydroxylamine; an alkyl-hydroxylamine; a

mercaptoalkylamine; a guanidine; a diaminoguanidine; an aminoguanidine; a cyanamide; an alkyl ester of an amino acid; a thiosemicarbazide or a semicarbazid or a saturated or unsaturated ether group, for example an alkoxy, a cycloalkoxy, an alkenoxy, a cycloalkenoxo, an alkadienoxo, an alkynoxo, an aryloxy group; a poly(oxy-alkylated) alkoxy group; an aliphatic ketoxime; a substituted saturated or un-saturated alkoxy group in which the substituents are for example halogens, dialkylamine, a heterocycyclic or heteroaromatic group, an alkylester of an alkyl carboxylic acid, a phosphonic ester, salt of a sulphonic acid, a sulphonic ester, or a sulphuric ester group.

X can be the residue of a compound with a carbon atom containing a reactive hydrogen, for example a dialkyl malonate; an acetoacetic ester; acetylacetone; diazomethane; hydrogen cyanide; a thiazoleum salt.

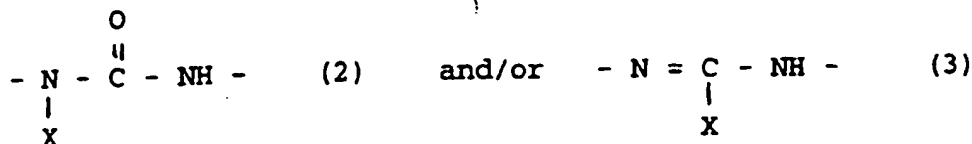
X in formula (3) can be hydrogen sulphide; an alkyl sulphide; an hydrogen selenide; or an alkyl selenide.

The value of p is at least 1 for polymeric compounds and in principle unlimited and depending on the application it can be between 0 and 50 for oligomeric materials. The ratio of q to p can be 0 and 20 and is preferably 0.2 to 5.

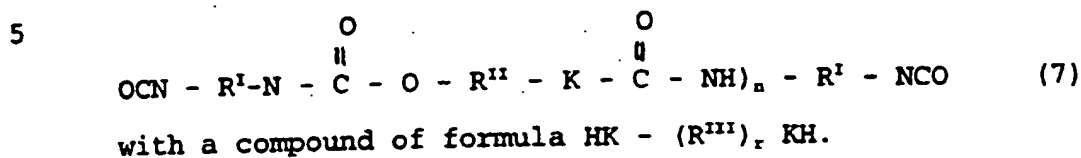
The mean value of m is 1 to 20 and is preferably 1 to 5.

The mean value of n is suitably 1 to 5, and preferably 1 to 2.

Polymers according to the invention may be made by polymerising as a dispersion in an aqueous medium a compound which comprises groups of formula



and also two -NCO groups, with a compound of formula

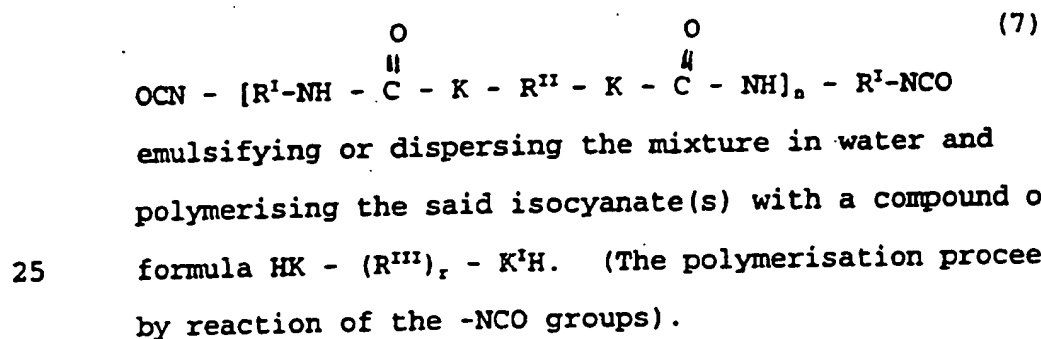


This process, because the polymer is formed in aqueous suspension, avoids the need to disperse the polymer into an aqueous phase in order to form dispersions according to the invention. The dispersion of a preformed polymer into an aqueous medium is difficult to achieve and may be impossible if the polymer has a high molecular weight.

Polymers according to the invention may be made by a process which comprises reacting a compound of formula

$$\text{OCN} - (\text{R} - \text{N} = \text{C} = \text{N})_n - \text{R} - \text{NCO} \quad (8)$$

with a carboxylic acid of formula HOX which may be substituted, optionally mixing the product with a compound of formula



Alternatively polymers according to the invention may be made by a process which comprises reacting the NCO functions of a compound of formula (8) with an excess of a compound of formula $\text{HK} - (\text{R}^{III})_r - \text{K}^I\text{H}$, under mild conditions, such that substantially no reaction with the

- N = C = N - groups occurs if the desired group X is not a - KR^{III} KH group and in that case reacting the product with a compound of formula HX or HOX having the desired group X, reacting the resulting product, optionally
5 together with a compound of formula HK - R^{II} - KH with a diisocyanate which may have the formula OCN-R-NCO and/or OCN-R^I-NCO to produce a product with terminal -NCO functions and polymerising it as a dispersion in an aqueous medium with a compound of formula HK (R^{III}), K^IH.

10 Suitably compound (8) may be prepared according to European Patent 507,407 by condensation polymerisation of isocyanate containing materials at elevated temperatures in the presence of suitable catalysts with the evolution of CO₂. Compound (8) may then be reacted with HX or HOX,
15 eg a carboxylic acid which may be substituted at temperatures between 20 and 100°C. Compound (7) is a conventional isocyanate terminated polyurethane prepolymer. It may be produced by known methods by the reaction of diols, aminoalkanols and/or diamines with
20 diisocyanates.

An NCO-capping agent for example an alkyl amine, a dialkylamine, an aminoalkanol or an di-(hydroxyalkyl)-amine may be present to shorten the chain length of the polymer.

25 Diisocyanates used in the process of the present invention can be saturated aliphatic diisocyanates, cyclo-aliphatic diisocyanates, aromatic diisocyanates, and in particular contain hydrocarbon groups having up to 20 carbon atoms, especially up to 15 carbon atoms. As
30 examples of suitable diisocyanates there may be mentioned 2,4-toluenediisocyanate, 2,6-toluenediisocyanate and

mixtures thereof, dicyclohexylmethane-4,4'-diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate, and 1,6-diisocyanatohexane.

The diol, diamine, amine or alkanol may provide the hydrophilic segments in the polymer, which eases the dispersibility of the polymer in water. The hydrophilic segments, which typically incorporate poly(oxyethylene) chains, may be in the main chain or may be in the side chains of the polymer. The compound may contain a poly(oxyalkylene) side chain containing an acid residue, for example a salt of a sulphonic acid. The hydrophilic diol, diamine, amine, or alkanol reacts with isocyanate groups to form a linkage of the type -NH(C=O)O- or NH(C=O)NH- between the hydrophilic group and, for example, a residue of a diisocyanate compound. Further an hydrophilic alkanol or amine can react with a carbodiimide function to form a trisubstituted isourea or guanidine, respectively. Particularly suitable hydrophilic diols, diamines, amines or alkanols contain poly(oxyalkylene) groups having a molecular weight of 100 to 10000; generally the molecular weight does not exceed 5000, and preferably the molecular weight is between 500 and 2000. Compounds having a poly(oxyalkyl) side chain include 2-(hydroxy-methyl)-2-(oxyalkylated)-butan-1-ol, 2-(oxyalkylated)-ethanol, 2-(oxyalkylated)-aminoethane, wherein the oxyalkylated groups may be poly(oxyethylene), or poly(oxyethylene)-poly(oxypropylene) block copolymer groups, either of which may contain an acid residue, in particular a sodium sulphonate group.

The diols used in the present invention to prepare the polyurethane prepolymer, to prepare the carbodiimide

containing oligomer, or for the chain extension may be alkanediols, alkenediols, cyclo-alkenediols, cyclo-alkenediols or aromatic diols or a mixture of these. The alkanediols may contain 1 to 30 and preferably 2 to 15 carbon atoms.

Suitably, the diols used in the present invention to prepare the polyurethane prepolymer or to prepare the carbodiimide oligomer may be polyols used for the preparation of polyurethane coating compounds. Suitable diols are polyoxyalkylene diols, for example one of which each alkylene group has 2 to 6 carbon atoms for example polyoxyethylene, polyoxypropylene or polyoxybutylene diol, or of an OH-terminated polyester chain, for example an aliphatic dicarboxylic acid/alkylene diol chain, an aromatic dicarboxylic acid/alkylene diol chain, a polcaprolactone, a polycarbonate/alkylene diol or a dimeric fatty acid/alkylene diol chain. The diols may have a molecular weight of 62 to 5000, preferably from 100 to 3000 and may be mixtures having mean molecular weights in this range.

To improve the water dispersibility part of the diol precursors to the polyurethane prepolymer can be the residue of an alkanediol with a side chain containing a carboxylic acid, a sulphonic acid or a sulphate, for example, dimethylolpropanoic acid or dihydroxybenzoic acid.

The diamines used in the preparation of the polyurethane prepolymer or for the chain extension may be the normal diamines used in the polyurethane chemistry to prepare coatings. Suitable diamines are for example hydrazine, diaminoalkanes, diaminocycloalkanes, diamino-

cyclalkenes, diaminoalkenes, diaminoalkynes, diaminoaryls, hydroxyalkyldiaminoalkanes. The diamino compounds may contain 1 to 30 and preferably 2 to 15 carbon atoms.

5 The aminohydroxy compounds used in the preparation of the polyurethane prepolymer or for the chain extension may be the normal aminohydroxy compounds used in the polyurethane chemistry to prepare coatings. Suitable compounds are for example aminoalkanols, aminocyclo-
10 alkanols, aminocyclalkenols, aminoalkenols, aminoalkynols and aromatic aminohydroxy compounds. The aminohydroxy compounds may contain 1 to 30 and preferably 2 to 15 atoms.

Agents to control the chain length of the polymer may be monovalent compounds which react with the NCO
15 function, for example aminoalkanes, dialkylamines, amino-alkanols, alkanols. To obtain water dispersibility the capping agent may contain carboxylic groups or tertiary aminofunctions, for example as in amino acids or dialkyl-aminoalkanol, or the capping agent may contain a poly-
20 (oxyalkyl) group.

The compound HOX or salt thereof may be a substituted carboxylic acid, for example, an unsaturated acid, for example acrylic acid, methacrylic acid, crotylic acid, sorbic acid, cinnamic acid;
25 methoxycinnamic acid, butynoic acid an unsaturated fatty acid, for example, oleic acid or linoleic acid linolenic acid or phytol; a saturated fatty acid, for example stearic acid, iso-stearic acid or palmitic acid; a perfluoro alkanolic acid, for example heptafluorobutanoic
30 acid, pentadecafluorooctanoic acid; an amino acid, for example alanine, β -alanine, glycine and the like; an

aldehyde functional carboxylic acid, for example, glyoxylic acid; a keto functional carboxylic acid, for example pyruvic acid or acetoacetic acid; an hydroxy functional acid, for example hydroxybutyric acid, or lactic acid; a poly(oxyalkylene) carboxylic acid, with a molecular weight between 200 and 3000.

Alternatively, compound HX may be ammonia or a substituted amine, for example a saturated or unsaturated fatty amine, for example octadecanoic amine or octadecenoic amine; a poly(oxyalkylene)amine with a molecular weight between 200 and 3000; hydrazine; alkylhydrazine; urea; alkylurea; an amino-alkyltri-alkoxysilane or an aminodi-(alkyltrialkoxysilane).

Alternatively, compound HX or salt thereof may be an aliphatic or aromatic alcohol for example ethanol, propanol, butanol, hexanol, fatty alcohol, borneol, phenol, picric acid, or a compound with a carbon containing a reactive hydrogen, for example alkyl acetoacetate, dialkylmalonate or acetylacetone, or preferably the sodium or potassium salts therefrom.

Compounds in which the group X contains olefinically unsaturated groups are photo-polymerisable by ultraviolet light in the presence of photoinitiators. Such photoinitiators include those sold under the Trade Names "Quantacure" types ABQ, BEA, BMS, BPQ, BTC, DMB, EPD, ITX, QTX (obtainable from Int. Bio-Synthetics), "Darocur" 1116, "Darocur" 1173 and "Darocur" 2959 (obtainable from Ciba Geigy), "Esacure" types EB 3, KB 1, TZT, KIP 100 F, ITX, EDB, X 15, KT 37 (obtainable from Fratelli Lamber-ti), "Irgacure" 184 and "Irgacure" 2959 (obtainable from Ciba Geigy). Such compounds are of particular interest in

surface coating applications, for example paints and varnishes.

5 The polymeric compounds are preferably water dispersible film forming polymers. After the formation of the films the polymers are resistant to redispersion in water. For applications where oligomeric compounds are desired, the chain length of the polymers of the invention can be adjusted by capping the terminal isocyanate groups with substituted amino or hydroxy compounds.

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Non reactive solvents may be used as desired in carrying out chemical reactions as aforesaid.

20 Compounds of the invention may be used as surface coatings for example for finishing or impregnating leather, artificial leather, wood, metal, glass, synthetic material, concrete, stone, paper, fabrics, eg woollen fabrics, rubber and other surfaces. They further can be used as binders or additives for inks, sealants, formulated paints, adhesives, varnishes and clear (unpigmented) coatings. Alternatively they can be used as reagents in tanning and retanning processes for leather. The aqueous dispersions may be applied onto surfaces, for example leather or leatherlike material by normal procedures. If X contains a long chain aliphatic

25

30

group the water resistance of the coated or impregnated material will be increased and the material will have a waxy feeling. If X contains a fluorinated alkyl chain, the material will become water repellant, oil resistant and stain resistant. If X contains double bonds a self crosslinkable coating will be obtained. The crosslinking can be initiated by radical initiators or by UV radiation. As a result the film properties may be improved; for example water and solvent resistance, abrasion resistance, film hardness, and wet-rubbing properties. If X contains alkoxysilane functions, the compound is selfcurable.

The emulsions may contain 2-60% by weight of the polymer, and preferably 10-40%. Many additional ingredients may be present in the emulsions, for example fillers, colorants, photoinitiators, radical initiators, levelling agents, thermal stabilisers, plasticisers, anti-oxidants, biocides, lubricating agents, water-proofing agents, silicones, additional curing agents and/or matting agents.

Various aspects of the present invention are illustrated by the following examples. The examples are illustrative of the invention and not limiting.

Examples

Example 1

Preparation of an oligomeric material containing carbodiimide functions and terminal isocyanate functions which is a precursor of RA in the general formula (1).

Under a nitrogen atmosphere a mixture of 222 g (1 mole) of 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate (isophoronediiisocyanate, hereafter

referred to as IPDI), 93.8 g (0.07 mole) of a 2-hydroxymethyl-2-(sodium sulphonate terminated oxy-alkylated [EO/PO weight ratio 85/15]-butane-1-ol (having a molecular weight of about 1340) and 1.8 g of 2,5-dihydro-3-methyl-1-phenyl-phosphol-1-oxide were heated to 150°C while stirring. Heating and stirring were continued until the isocyanate amount was 11 - 12 % by weight of the reaction mixture. 125 g of N-methylpyrrolidnone (hereafter referred to as NMP) was added and the mixture was cooled down to room temperature. The solids amount of the final mixture was 70% and the NCO amount was 7.81%. The product was used in Example 3 up to and including 14 and in Example 18, 19 and 20.

Example 2

Preparation of an oligomeric material containing carbodiimide functions and terminal isocyanate functions which is a precursor of RA in the general formula (1).

The procedure of Example 1 was repeated with the exception that the reaction mixture was reacted till an NCO amount of 7-7.5% and 122 g of NMP was used to dilute the reaction mixture to a solids amount of 70%. The NCO amount was 4.80%. The product was used in Example 15, 16 and 17.

Example 3-17

Reaction of an oligomeric material containing carbodiimide functions and terminal isocyanate functions with substituted carboxylic acids.

100 g of the product of Example 1 or 2 (carbodiimide functionality: 130 meq and 171 meq respectively) was heated to 50°C. A mixture of a substituted carboxylic acid (0.9 equivalent) and NMP (the mixture has a solids

amount of 70%), as referred to in Table I, were added while stirring. After stirring for 30 min the mixture was cooled down. Analysis by IR-spectroscopy showed that the carbodiimide functions had disappeared completely or almost completely. Functionalised polymers were obtained by the chain extension of a mixture of each product and a polyurethane prepolymer as described in Examples 21 up to and including 41.

Table I

Example No	Carboxylic acid + product of Example	Carb-oxylic acid Weight	NMP Wght	Product is further used in Example
3	Acrylic 1	8.42	3.61	21-22-23-38-39-40-41-42-43
4	Methacrylic 1	10.06	4.31	24
5	Crotonic 1	10.06	4.31	25
6	Sorbic 1	13.10	5.61	26
7	Cinnamic 1	17.32	7.42	27
8	Oleic 1	33.05	14.16	28
9	Stearic 1	33.29	14.27	29-44-45
10	Isostearic 1	33.29	14.27	30
11	Heptafluoro butyric 1	25.04	10.73	31
12	Pentadecafluoro octanoic 1	48.44	20.76	32
13	Glyoxylic 1	10.77	4.62	33
14	Polyethoxyethyl (mw 1200) 1	140.4	60.17	34
15	Acrylic 2	11.08	4.75	35
16	Methacrylic 2	13.23	5.67	36
17	Stearic 2	43.79	18.77	37

20

Example 18

Preparation of an aqueous polyurethane dispersion, functionalised with hydrophilic groups.

5.67 g (93 mmole) of ethanolamine in 2.43 g of NMP was added to 50 g of the product of Example 1 (contains

93 mmole of isocyanate) at 20°C while stirring. After stirring for 30 min the mixture was heated to 80°C and a mixture of 68.74 g (58.5 mmole) 2-amino-1-oxyalkylated [PO/EO weight ratio 1.6/18.6]-propane (molecular weight 1175) and 29.46g of NMP was added while stirring. The mixture was reacted for 2 h at 80°C. Analysis by IR-spectroscopy showed that the carbodiimide signal had disappeared almost completely. 154.28 g (165 mmole) of a polyester diol based on neopentylglycol, caprolactone and adipic acid (having a mean molecular weight of 935) was added and the mixture was heated to 70°C, while stirring. 89.24 g (402 mmole) of IPDI was added and the temperature was increased to 100°C. 0.1 g of tin octoate was added as a catalyst. After reacting for 2 hrs at 100°C the reaction mixture was cooled down to 20°C. The NCO-amount of the product was 4.00 (total: 381 meq of NCO). To emulsify the reaction mixture, 1026 g of water was added while stirring intensively, immediately followed by 9.05 g (181 mmole) of hydrazine hydrate in 30g of water. The mixture was stirred for another 30 minutes.

Example 19

Preparation of an aqueous polyurethane dispersion, functionalised with hydrophobic groups.

5.67 g (93 mmole) of ethanolamine in 2.43 g of NMP was added to 50 g of the product of Example 1 (contains 93 mmole of isocyanate) at 20°C while stirring. After stirring for 30 min the mixture was heated to 80°C and a mixture of 16.26 g (58.5 mmole) of a fatty amine (a mixture of C16, C17 and C18 fatty amines with a ratio of 8.5/1.5/90 and a mean molecular weight of 278) and 13.9 g of NMP was added while stirring. The mixture was reacted

for 2h at 80°C. Analysis by IR-spectroscopy showed that the carbodiimide signal had disappeared almost completely. 46.6 (23.3mmole) of a polypropyleneglycol (molecular weight 2000) and 10.02 g (74.8 mmole) of 2,2-dihydroxymethylpropanoic acid were added and the mixture was heated to 70°C, while stirring. 61.05 g (275 mmole) of IPDI was added and the temperature was increased to 100°C. 0.1 g of tinocatoate was added as a catalyst. After reacting for 2 hrs at 100°C the reaction mixture was cooled down to 20°C. The NCO-amount of the product was 5.02 (total: 246 meq of NCO). 7.52 g of triethylamine was added and the mixture was stirred until homogeneous. To emulsify the reaction mixture, 473.5 g of water was added while stirring intensively, immediately followed by 5.85 g (117 mmole) of hydrazine hydrate in 40 g of water. The mixture was stirred for another 30 minutes.

Example 20

Preparation of an aqueous polyurethane dispersion, in which the polyurethane is functionalised with alkoxysilane functions.

5.67 g (93 mmole) of ethanolamine in 2.43 g of NMP was added to 50 g of the product of Example 1 (contains 93 mmole of isocyanate) at 20°C while stirring. After stirring for 30 min the mixture was heated to 80°C and a mixture of 10.47 g (58.5 mmole) of 1-amino-3-(trimethoxysilyl)-propane and 4.5 g of NMP was added while stirring. The mixture was reacted for 2 h at 80°C. Analysis by IR-spectroscopy showed that the carbodiimide signal had disappeared almost completely. 93.0 (46.5 mmole) of a polypropyleneglycol (molecular weight 2000) and 12.46 g (93 mmole) of 2,2-dihydroxymethylpropanoic

acid were added and the mixture was heated to 70°C, while stirring. 78.46 g (353.4 mmole) of IPDI was added and the temperature was increased to 100°C. 0.1 g of tinooctoate was added as a catalyst. After reacting for 2
5 hrs at 100°C the reaction mixture was cooled down to 20°C. The NCO-amount of the product was 5.10 (total: 312 meq of NCO). 9.35 g of triethylamine was added and the mixture was stirred until homogeneous. To emulsify the reaction mixture, 658.4 g of water was added while
10 stirring intensively, immediately followed by 7.41 g (148 mmole) of hydrazine hydrate in 20 g of water. The mixture was stirred for another 30 minutes.

Example 21-35

Preparation of aqueous polyether polyurethane
15 dispersions, in which the polyurethane has functionalised side chains.

A mixture of 450 g (225 mmole) of a polypropylene glycol (having a mean molecular weight of 2000), 36.85 g (275 mmole) of 2,2-dihydroxymethylpropanoic acid and
20 77.52 g of NMP was heated to 70°C, while stirring. 210.9 g (950 mmole) of IPDI was added and the temperature was increased to 100°C. 0.1 g of tinooctoate was added as a catalyst. After reacting for 2 hrs at 100°C the reaction mixture was cooled down to 20°C. The NCO-amount of the
25 product was 4.39 (total: 810 meq of NCO). A product of Example 3-17 was added, as referred to in Table II and the mixture was stirred until homogeneous. 27.62 g of triethylamine was added (Table II) and the mixture was stirred until homogeneous. To emulsify the reaction
30 mixture, an amount of water was added (Table II) while stirring intensively, immediately followed by an amount

of hydrazine hydrate (0.9 equivalent regarding to the NCO amount as referred to in Table II) in 70 g of water. The mixture was stirred for another 30 minutes. The final solids amounts were 25%.

5 The testing results of the curing by UV radiation of the films of the double bond containing products from Examples 21, 22, 23, 24, 33 and 34 are presented in Example 46.

10 The testing results of the hydrophobic properties of the films of the products containing a long alkyl side chain or a fluoralkyl side chain from Examples 26, 27, 28, 29 and 30 are presented in Example 48.

Table II

Example	added product from Example	amount of added product		amount of hydrazine hydrate		amount of wa-ter
		meq NCO	g	mmole	g	g
21	3	610	367.5	675	33.73	2629
22	4	610	374.2	675	33.73	2642
23	5	610	374.2	675	33.73	2642
24	6	610	388.5	675	33.73	2667
25	7	610	409.4	675	33.73	2705
26	8	610	484.1	675	33.73	2839
27	9	610	484.1	675	33.73	2839
28	10	610	484.1	675	33.73	2839
29	11	100	73.0	432	21.60	2130
30	12	100	90.1	432	21.60	2222
31	13	610	378.9	675	33.73	2650
32	14	350	366.5	551	27.55	2650
33	15	360	364.7	556	27.79	2618
34	36	360	374.2	556	27.79	2635
35	37	360	512.8	556	27.79	2954

20

Example 36

Preparation of an aromatic aqueous polyether polyurethane dispersion with side chains containing a double bond.

25

A mixture of 450 g (225 mmole) of a polypropylene glycol with a molecular weight of 2000, 36.85 g (275

mmole) of 2,2-dihydroxymethylpropanoic acid and 72.46 g of NMP was heated to 70°C, while stirring. 165.3 g (950 mmole) of toluene diisocyanate was added and the temperature was increased to 95°C. After reacting for 2
5 hrs at 95°C the reaction mixture was cooled down to 20°C. The NCO-amount of the product was 4.80 (total: 828 meq of NCO). 301.2 g of the product of Example 3 (containing 500 meq of NCO) was added and the mixture was stirred until homogeneous. 27.66 g of triethylamine was added and the
10 mixture was stirred until homogeneous. To emulsify the reaction mixture, 2377 g of water was added while stirring intensively, immediately followed by 31.54 g (631 mmole) of hydrazine hydrate in 70 g of water. The mixture was stirred for another 30 minutes.

15 **Example 37**

Preparation of an aqueous polyester polyurethane dispersion with side chains containing a double bond.

A mixture of 116.88 g (125 mmole) and of 304.00 g (100 mmole) of polyester diols based on neopentyl-glycol, caprolactone and adipic acid (having a mean molecular
20 weight of 935 and 3040 respectively), of 36.85 g (275 mmole) of 2,2-dihydroxymethylpropanoic acid and of 74.29 g of dipropylene glycol dimethyl ether was heated to 70°C, while stirring. 210.9 g (950 mmole) of IPDI was
25 added and the temperature was increased to 100°C. 0.1 g of tinocatoate was added as a catalyst. After reacting for 2 hrs at 100°C the reaction mixture was cooled down to 20°C. The NCO-amount of the product was 4.83 (total: 854 meq of NCO). 361.45 g of the product of Example 3
30 (containing 600 meq of NCO) was added and the mixture was stirred until homogeneous. 27.64 g of triethylamine was

added and the mixture was stirred until homogeneous. To emulsify the reaction mixture, 2538 g of water was added while stirring intensively, immediately followed by 34.53 g (691 mmole) of hydrazine hydrate in 70 g of water. The mixture was stirred for another 30 minutes. The testing results of the UV-curing of the product applied onto leather is presented in Example 47.

Example 38

Preparation of an aqueous polyester polyurethane dispersion with side chains containing a double bond. A mixture of 459 g (225 mmole) of a polycaprolactone diol with a mean molecular weight of 2040), 36.85 g (275 mmole) of 2,2-dihydroxymethylpropanoic acid and 78.53 g of dipropylene glycol dimethyl ether was heated to 70°C, while stirring. 210.9 g (950 mmole) of IPDI was added and the temperature was increased to 100°C. 0.1 g of tinooctoate was added as a catalyst. After reacting for 2 hrs at 100°C the reaction mixture was cooled down to 20°C. The NCO-amount of the product was 4.57 (total: 855 meq of NCO). 361.45 g of the product of Example 3 (containing 600 meq of NCO) was added and the mixture was stirred until homogeneous. 27.62 g of triethylamine was added and the mixture was stirred until homogeneous. To emulsify the reaction mixture, 2649g of water was added while stirring intensively, immediately followed by 34.56 g (691 mmole) of hydrazine hydrate in 70 g of water. The mixture was stirred for another 30 minutes.

Example 39

Preparation of an aqueous polyether polyurethane dispersion with side chains containing a double bond. A mixture of 440 g (220 mmole) of a polybutylene glycol

with a mean molecular weight of 2000, 37.52 g (280 mmole) of 2,2-dihydroxymethylpropanoic acid and 75.26 g of dipropylene glycol dimethyl ether was heated to 70°C, while stirring. 199.8 g (900 mmole) of IPDI was added and the temperature was increased to 100°C. 0.1 g of tinocatoate was added as a catalyst. After reacting for 2 hrs at 100°C the reaction mixture was cooled down to 20°C. The NCO-amount of the product was 4.67 (total: 837 meq of NCO). 361.45g of the product of Example 3 (containing 600 meq of NCO) was added and the mixture was stirred until homogeneous. 28.17 g of triethylamine was added and the mixture was stirred until homogeneous. To emulsify the reaction mixture, 2642 g of water was added while stirring intensively, immediately followed by 71.10 g (683 mmole) of 2-aminoethylethanolamine in 150 g of water. The mixture was stirred for another 30 minutes. The testing results of the UV-curing of the product applied onto leather is presented in Example 47.

Example 40

Preparation of an aqueous polyester polyurethane dispersion with side chains containing a double bond.

A mixture of 448.8 g (220 mmole) of a hexane-dioldipate dimerate diol, with a mean molecular weight of 2040, 37.52 g (280 mmole) of 2,2-dihydroxymethylpropanoic acid and 76.24 g of dipropylene glycol dimethyl ether was heated to 70°C, while stirring. 199.8 g (900 mmole) of IPDI was added and the temperature was increased to 100°C. 0.1 g of tinocatoate was added as a catalyst. After reacting for 2 hrs at 100°C the reaction mixture was cooled down to 20°C. The NCO-amount of the product was 4.61 (total: 837 meq of NCO). 361.45 g of the

product of Example 3 (containing 600 meq of NCO) was added and the mixture was stirred until homogeneous. 28.13 g of triethylamine was added and the mixture was stirred until homogeneous. To emulsify the reaction mixture, 2668 g of water was added while stirring intensively, immediately followed by 71.10 g (683 mmole) of 2-aminoethylethanolamine in 150 g of water. The mixture was stirred for another 30 minutes.

Example 41

10 Preparation of an aqueous polycarbonate polyurethane dispersion with side chains containing a double bond.

A mixture of 440.0 g (220 mmole) of a polycarbonate diol, with a mean molecular weight of 2000, 37.52 g (280 mmole) of 2,2-dihydroxymethylpropanoic acid and 75.26 g of dipropylene glycol dimethyl ether was heated to 70°C, while stirring. 199.8 g (900 mmole) of IPDI was added and the temperature was increased to 100°C. 0.1 g of tin octanoate was added as a catalyst. After reacting for 2 hrs at 100°C the reaction mixture was cooled down to 20°C. The NCO-amount of the product was 4.52 (total: 810 meq of NCO). 361.45 g of the product of Example 3 (containing 600 meq of NCO) was added and the mixture was stirred until homogeneous. 28.17 g of triethylamine was added and the mixture was stirred until homogeneous. To emulsify the reaction mixture, 2658 g of water was added while stirring intensively, immediately followed by 69.77 g (670 mmole) of 2-aminoethyl-ethanolamine in 150 g of water. The mixture was stirred for another 30 minutes. The testing results of the UV-curing of the product applied onto leather are presented in Example 47.

Example 42

Preparation of an aqueous dispersion of a urethane oligomer with hydrophobic side chains.

111 g (500 mmole) of IPDI was added to a mixture of
5 33.50 g (250 mmole) of 2,2-dihydroxy-methylpropanoic acid
and 77.81 g of NMP, while stirring. The temperature was
slowly increased to 70°C. After reacting for 2 hrs at
70°C the reaction mixture was cooled down to 20°C. The
NCO-amount of the product was 8.88 (total: 470 meq of
10 NCO). 198.41 g of the product of Example 9 (containing
250 meq of NCO) was added and the mixture was stirred
until homogeneous. 16.25 g of triethylamine was added and
the mixture was stirred until homogeneous. To emulsify
the reaction mixture, 717.62 g of water was added while
15 stirring intensively, immediately followed by a mixture
of 12.00 g (240 mmole) of hydrazine hydrate and 14.64
(0.240 mole) of aminoethanol in 40 g of water. The
mixture was stirred for another half hr. The testing
results of the hydrophobic properties of the product are
20 presented in Example 49.

Example 43

Preparation of an aqueous dispersion of a urethane oligomer with hydrophobic side chains.

The procedure of Example 42 was repeated with the
25 exception that 704 g of water was used to emulsify the
reaction mixture, and a mixture of 14.4 g (288 mmole) of
hydrazine hydrate and 8.78 g (144 mmole) of aminoethanol
in 40 ml water were used for the chain extension and
capping respectively. The testing results of the
30 hydrophobic properties of the product are presented in
Example 49.

Example 44

Preparation of a nonionic aqueous polyurethane dispersion with amino functional side chains.

5 A mixture of 374 g (400 mmole) of a polyester diol based on neopentylglycol, caprolactone and adipic acid (having a mean molecular weight of 935), and of 133.6 g (100 mmole) of a 2-hydroxymethyl-2-(sodium sulphonate terminated oxyalkylated [EO/PO weight ratio 85/15]-butane-1-ol (having a molecular weight of about 1340) and
10 of 126.8 g of NMP (was heated to 70°C, while stirring. 210.9 g (950 mmole) of IPDI was added and the temperature was increased to 100°C. 0.1 g of tin octanoate was added as a catalyst. After reacting for 2 hrs at 100°C the reaction mixture was cooled down to 20°C. The NCO-amount
15 of the product was 3.97 (total: 801 meq of NCO). 376.3 g of the product of Example (1) was added (containing 700 meq of NCO) and the mixture was stirred until homogeneous. To emulsify the reaction mixture, 2692 g of water was added while stirring intensively, immediately
20 followed by 35.6 g (712 mmole) of hydrazine hydrate in 70 g of water. The mixture was stirred for another 30 minutes. A mixture of 39.18 g of B-alanine in 137 g of 2 N HCl was added and the mixture was stirred for another 30 minutes. The dispersion was adjusted to pH 8 with
25 triethylamine. The testing results of the crosslinking properties of the product are presented in Example 50.

Example 45

Preparation of an oligomeric material with side chains containing a double bond.

30 The procedure of Example I was repeated with the exception that the reaction was executed in 154 g of

methoxypropanol and the mixture was reacted until an NCO amount of 5.5, and 126.9 g of NMP was used to dilute the reaction mixture to a solids amount of 50%. After the cooling down the NCO amount was 3.85 %. 43.05 g of dimethylethanolamine in 43.05 g of NMP was added at 70°C and the mixture was stirred for 1 h at 70-80°C. The mixture was cooled down to 50°C. 43.26 g (601 mmole) of acrylic acid was added and the mixture was stirred for 30 minutes and cooled down. The double bond functionality is 0.90 meq/g. The product is used in Example 46.

Example 46

Evaluation of the crosslinking properties of the products of Examples 21, 22, 23, 24, 33, 34 and 45.

This example illustrates the effect of the curing by ultraviolet radiation on the film properties of the products of Examples 21, 22, 23, 24, 33 and 34, and the effect of the presence of the product of Example 45, which enhances the double bond concentration.

1.88 g of a 20 % solution of photoinitiator in water or NMP was mixed with 50 g of the products of Examples 21, 22, 23, 24, 33 or 34. To increase the double bond functionality, the product of Example 45 was added in an amount as referred to in Table III. (1 equivalent of extra double bonds) Films of 200 micrometer were prepared and dried at 70°C. The films were cured by UV radiation at a wave length of 240 nm and 2000 mJ/cm² total energy. The swelling percentages in ethanol and the melting points of the cured and uncured films were measured. The results are presented in Table III.

The results show that the modified polyurethanes of the invention containing side chains with double bonds

can be cured by UV light and that the addition of a compound with additional double bonds enhances the crosslinking density as indicated by:

- non-cured films gel in alcohol, while UV-cured films remain intact and just swell.
- A lower uptake of alcohol by UV-cured films is observed in the presence of a compound with additional double bonds (product of Example 45).
- an increased melting point is obtained when the films are cured.
- a more increased melting point is obtained in the presence of a compound with additional double bonds (product of Example 45).

Table III

Product of Example	amount of prod. of ex. 45 (g) ^{a)}	Photo-initiator ^{b)}	UV ^{c)} curing	weight increase ^{d)} (%)	decomposition point ^{e)} (°C)
21	-	Esacure	-	g	190
21	-	Esacure	+	310	210
21	-	Quantac.	-	g	190
21	-	Quantac.	+	290	210
21	-	Darocur 2	-	g	190
21	-	Darocur 2	+	260	210
21	-	Darocur 1	-	g	190
21	-	Darocur 1	+	290	210
21	5.2	Darocur 1	+	240	220
22	-	Darocur 1	+	360	200
22	5.2	Darocur 1	+	300	210
23	-	Darocur 1	+	370	200
24	-	Darocur 1	+	480	200
33	-	Darocur 1	+	280	210
34	-	Darocur 1	+	370	200

a) An amount of the product of Example 45 is added which corresponds to one additional equivalent of

double bonds.

- b) The types of photoinitiator are respectively:
Esacure: Esacure KIP 100F; Quantac.: Quantacure BTC;
Darocur 2: Darocur 2959; Darocur 1: Darocur 1116.
- 5 c) The films of the products are cured (+) or uncured (-) by UV radiation.
- d) Weight increase is the proportional weight increase of a film drawn at 200 micrometer and which after drying and curing has lain in alcohol for 20 min at
- 10 20°C; g means that the film becomes a gel.
- e) The decomposing point of the films is measured on a Kofler bank type WME. Above the temperature mentioned the film becomes brittle.

Example 47

- 15 Evaluation of the crosslinking properties of the products of Examples 37, 39, 41, applied onto leather.

This example illustrates the effect of the curing by ultraviolet radiation on the products of Examples 37, 39, and 41 when applied onto leather. To obtain a homogeneous

20 coating the products were formulated as follows:

product from Example	100 g
thickening agent	1 g
levelling agent	1.5 g
matting agent	5 g
25 silicon feel agent	5 g
photoinitiator	1.4 g

The products were sprayed on precoated bovine grain leather with a layer thickness of 25 micro-meter. The coated leather was dried for 2 min at 70°C and cured by

30 UV radiation at a wave length of 240 nm and 2000 mJ/cm² total energy. The leather was subjected to a wet rub

test. The results showing the number of rubs required to damage the coating of the leather are presented in Table IV.

Table IV

5	Product from Example	UV-curing	Wet rubs
	37	-	25
	37	+	> 1000
	39	-	50
	39	+	350
10	41	-	30
	41	+	600

The results show that the polymeric coatings on the leather can be cured by UV-radiation as indicated by the much higher number of wet rubs which can be applied before the coating on the leather is damaged.

Example 48

Evaluation of the hydrophobic properties of the products of Examples 26, 27, 28, 29 and 30.

This example illustrates the hydrophobic properties which are obtained when a polyether urethane contains additional hydrophobic groups in the side chains.

To obtain a homogeneous coating the products were formulated as follows:

25	product from Example	100 g
	water	50 g
	thickening agent	2 g
	levelling agent	1.5 g
	silicon feel agent	5 g

The products were sprayed on bovine grain leather with a layer thickness of 2 times 25 micrometer. The coated leather was dried for 2 min at 70°C and tested for

its hydrophobic properties: the time needed for water to penetrate the coated leather was measured by a Bally Penetrometer. A polyether urethane, available from Stahl Holland as RU-4385 was used as a reference. The results of the test are presented in Table V.

Table V

Product	Time to penetrate leather (h)
uncoated leather	0.1
RU-4385	0.5
Example 26	5
Example 27	6
Example 28	6
Example 29	4
Example 30	8

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The results show that the presence of hydrophobic side chains in the polymer chains enhance the hydrophobic properties of coated leather, as indicated by the longer time it takes for water to penetrate the coated leather. This counts for both, the long alkyl side chains and the fluorinated side chains.

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Example 49

Evaluation of the hydrophobic properties of the products of Examples 42 and 43.

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This example illustrates the hydrophobic properties which are obtained when wet blue bovine grain leather is treated with the products of Example 42 or 43.

A piece of 30 g of wet blue bovine grain leather was impregnated for three h at 35°C with 100g of a dilution

of the product of Example 42 or 43 in water with a solids content of 5%. The leather was dried overnight at ambient temperature and tested for its hydrophobic properties: the time needed for water to penetrate the impregnated leather was measured by a Bally Penetrometer. A retanning agent available from Stahl Holland as Renektan QS was used as a reference. The results are presented in Table VI.

Table VI

Product	Time to penetrate leather (h)
leather (not impregnated)	0.1
Renektan QS	0.2
Example 42	2
Example 43	2.5

The results show that the presence of hydrophobic side chains in the polymer chains enhance the hydrophobic properties of impregnated leather as indicated by the longer time it takes for water to penetrate the impregnated leather.

Example 50

Evaluation of the crosslinking of the product of Example 44.

This example illustrates that a polyurethane with primary amine functions in the side chains can be crosslinked by an isocyanate crosslinker. As crosslinker was used EX-5193 available from Stahl Holland.

5.5 g of the crosslinker was diluted with 5.5 g of water and the mixture was stirred into 50 g of the

product of Example 44. A film of 200 micrometer was prepared and dried at 50°C for 30 minutes. The swelling percentage in alcohol was measured. The product of Example 44 without crosslinker was used as reference.

5 The result is presented in Table VII.

Table VII

Crosslinker in product of Example 44	Weight increase (%) ^{a)}
-	g
EX-5193	163

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a) Weight increase is the proportional weight increase of a film drawn at 200 micrometer and which after drying and curing has lain in alcohol for 20°C; g means that the film becomes a gel.

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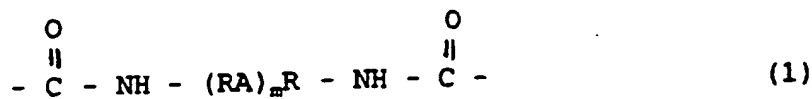
The result show that the amino functional product of Example 44 is crosslinkable by an isocyanate crosslinker as indicated by the much lower uptake of alcohol as indicated by:

20

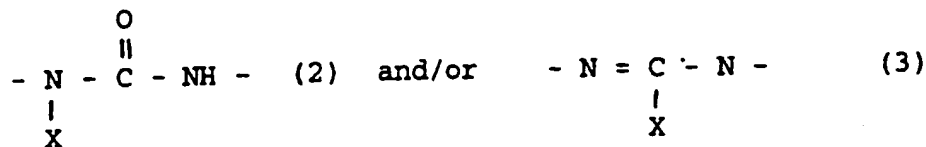
- a non-cured film gels in alcohol, while a crosslinked film remains intact and just swells.

Claims

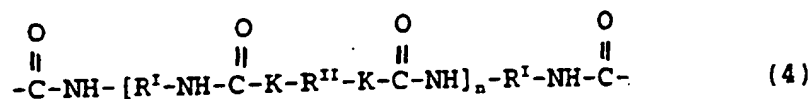
1 A functionalised polymer which comprises repeat units of formula YW and optionally ZV in which p groups of formula YW and q groups of formula ZV are present, in which Y is of formula



in which A is



in which Z is



in which V and W individually have the formula



wherein

YW and ZV may be present in any order and may be arranged as randomly or as blocks.

R, R^I, R^{II} and R^{III} are independently divalent organic groups which are unreactive towards other functions present in the molecule,

K is NH or O,

X is a property modifying group.

hydrophilic groups are present in R, R^I, R^{II}, R^{III} and/or X.

the ratio of q to p has a value from zero up to twenty and p is at least one,

m has a value from one up to twenty,

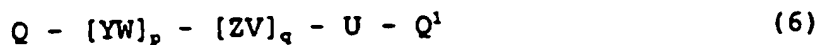
n has a value from half up to ten,

r has a value from 0 or 1 with the proviso that if r=0, K

is -NH, and

p and q and m and n represent statistical mean values and thus need not be integers.

2 A polymer as claimed in Claim 1 which has the general formula:



wherein U is Y or Z,

Q and Q¹ are individually groups of formula OR^A, NHR^A, or NR^AR^B and R^A and R^B are individually H, hydrocarbyl or substituted hydrocarbyl,

and p has a value from zero to 50 and when p is zero U is Y.

3 A polymer as claimed in Claim 1 or 2 wherein the group R^I, R^A or R^B contains a carboxylic acid, a sulphonic acid, or a sulphuric acid function or the corresponding salts.

4 A polymer as claimed in Claim 1, 2 or 3 wherein at least one of the groups R, R^I, R^{II}, R^{III}, R^A, R^B or X contains a hydrophilic segment which may be a polyoxyalkylene and preferably a polyoxyethylene, possibly containing a sulphonic acid residue.

5 A polymer as claimed in any of Claims 1 - 4 with a molecular weight of at least 1000.

6 A self-filmforming polymer as claimed in any of claims 1 and 3-5 with a molecular weight of at least 10,000 and preferably at least 20,000.

7 A polymer as claimed in any of Claims 1 to 6 wherein the groups R, R^I, R^{II}, R^{III}, R^A and R^B are hydrocarbon groups which are optionally substituted.

8 A polymer as claimed in Claim 7 wherein the groups R, R^I, R^{II}, R^{III}, R^A and R^B contain between 1 to 30 carbon

atoms.

9 A polymer as claimed in Claim 1-8 wherein the groups R, R^I, R^{II}, R^{III}, R^A and R^B are alkyl, alkenyl, cycloalkyl, cycloalkenyl, or aryl functions, which are optionally substituted by substituents which do not interfere in the polymer preparation and in the chemistry of the final product.

10 A polymer as claimed in Claim 9 wherein the hydrophilic segment in group R is the residue of an addition product of an isocyanate containing material and a poly(oxyalkylene) diol, a poly(oxyalkylene) diamine, a diol or diamine with a poly(oxyalkylene) side chain containing a sulphonic acid residue, from which the remaining isocyanate functions contribute to the carbodiimide formation, whereafter the carbodiimide functions are further reacted to the -NX-(C=O)-NH- or -N=C(X)-NH groups.

11 A polymer as claimed in any of Claims 1-10 wherein R^{II} is a residue of a polyoxyalkylene diol, from which the OH functions have reacted with an isocyanate containing material to form an urethane bond.

12 A polymer as claimed in Claim 11 wherein R^{II} is a residue of a polyoxyethylene, a polyoxypropylene, a polyoxybutylene diol.

13 A polymer as claimed in Claim 1-10 wherein R^{II} is a residue of a polyester diol, from which the OH functions have reacted with an isocyanate containing material to form a urethane bond.

14 A polymer as claimed in Claim 13 wherein R^{II} is a residue of an aliphatic dicarboxylic acid/alkylene diol ester diol, an aromatic dicarboxylic acid/alkylene diol

ester diol, a polycaprolactone diol, a dimeric fatty acid/alkylene diol ester diol, a polycarbonate/alkylene diol ester diol.

15 A polymer as claimed in Claim 1-14 wherein R^1 is of the residue of an alkane diol containing a carboxylic acid, a sulphonic acid or a sulphate, from which the OH functions have reacted with an isocyanate containing material to form an urethane bond.

16 A polymer as claimed in Claim 1-15 wherein X in formula (2) is a substituted acyl function in which the substituent is an alkyl, a cycloalkyl, an alkenyl, a cycloalkenyl, an alkadienyl, an alkynyl, an aryl, or a fluorinated or halogenated alkyl or aryl group; a substituted saturated or unsaturated alkyl or cycloalkyl group, substituted by an amino, an alkylamino, a dialkylamino, a trialkylammonium, an alkoxy, an hydroxy, a thio, an oxo, an heterocyclo, an heteroaromatic, a phosphonic ester, salt of a sulphonic acid, a sulphonic ester, a sulphuric acid, a sulphuric ester or a poly(oxyalkylated) group.

17 A polymer as claimed in Claim 1-15 wherein X in formula (3) is a primary amine; an alkyl-, cycloalkyl-, alkenyl-, cycloalkenyl-, alkadienyl-, alkynyl-, alkanol-, thioalkyl-, aryl-amine; a poly(oxyalkylated) amine; a substituted alkylamine, substituted by an alkylamine, a dialkylamine, an alkoxy, an heterocyclic group, a heteroaromatic group, an alkoxysilane; an urea; a thiourea, an alyl urea; an alyl thiourea; an hydrazine, an alkylhydrazine, an acetoxylhydrazine, a carbethoxyhydrazine, an hydroxylamine; an alkyl-hydroxylamine; a mercaptoalkylamine; a guanidine; a

diaminoguanidine; an aminoguanidine; a cyanamide; an alkyl ester of an amino acid; an alkylaminoalkyl amine; a thiosemicarbazide; or a semicarbazid.

18 A polymer as claimed in Claim 1-15 wherein X in formula (3) is an alkoxy, a cycloalkoxy, an alkenoxy, a cycloalkenoxo, an alkadienoxo, an alkynoxo, an aryloxy group; a poly(oxy-alkylated) alkoxy group; an aliphatic ketoxime, a substituted saturated or unsaturated alkoxy group in which the substituents are halogens, dialkylamine, a heterocyclic or heteroaromatic group, an alkylester of an alky carboxylic acid, a phosphonic acid, salt of a sulphonic acid, a sulphonic ester, a sulphuric acid or a sulphuric ester group.

19 A polymer as claimed in Claim 1-15 wherein X in formula (3) is the residue of a dialkyl malonate; an acetoacetic ester; acetylacetone; diazomethane; hydrogen cyanide; or a thiazolium salt.

20 A polymer as claimed in Claim 1-15 wherein X in formula (3) is an hydrogen sulphide; an alkyl sulphide; an hydrogen selenide; or an alkyl selenide.

21 A polymer as claimed in Claim 16 wherein X in formula (2) is a acryloyl, a methacryloyl, a crotyloyl, a sorbyloyl, a cinnamoyl, methoxycinnamoyl, a octadecanoyl, an iso-octadecanoyl, an octadecenoyl, an hexadecanoyl, a hexadecenoyl, an octadecadienoyl, a hexadecadienoyl, a heptafluorobutanoyl, a pentadecafluoro-octanoyl, a glyoxyloyl, a 2-aminoacetyl, a 3-aminoacetyl a poly[(ethoxy/propoxy)acetyl or a polyethoxyacetyl function.

22 A polymer as claimed in Claim 17 wherein X in formula (3) is a fatty amine, 3-trimethoxysilylpropyl-

amine, 3,3-di(trimethoxysilyl)propylamine, 3-triethoxysilylpropylamine, a poly-ethoxy/propoxy)ethylamine or a poly-ethoxyethylamine.

23 A polymer as claimed in Claim 1-13 wherein the ratio of q to p is 0.2 to 5.

24 A polymer as claimed in claim 1-14 wherein the mean value of m is 1 to 5.

25 A polymer as claimed in claim 1-25 wherein the mean value of n is suitably 1 to 5 and preferably 1 to 2.

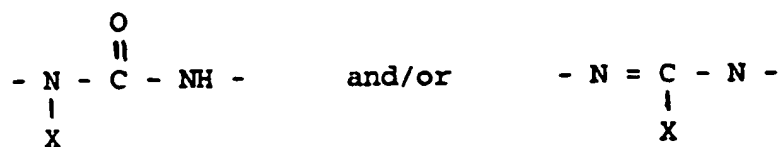
26 A self-crosslinkable polymer with side chains containing double bonds as claimed in Claim 1-21, 23-25 from which the crosslinking can be initiated by radical initiators and/or by UV-radiation.

27 A hydrophobic polymer with long alkyl side chains or fluorinated side chains as claimed in Claim 1-21, 23-25.

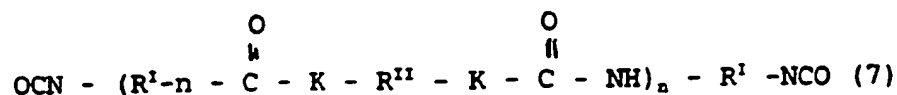
28 A self-crosslinkable polymer with alkoxysilane functional side chains as claimed in Claim 1-15, 17 and 22-25.

29 An aqueous emulsion or dispersion which comprises a polymer as claimed in any preceding claim.

30 A process of producing a polymer as claimed in any preceding claim as a dispersion in water which comprises polymerising as a dispersion in an aqueous medium a compound which comprises groups of formula

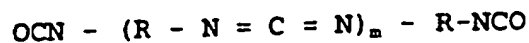


and also two -NCO groups, optionally together with a compound of formula

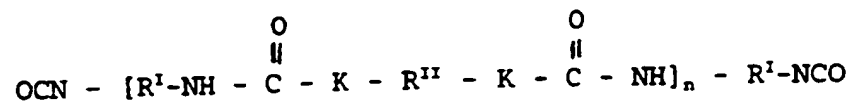


optionally in the presence of a tertiary amine, with a compound of formula $HK (R^{III})_x K^IH$.

31 A process according to Claim 30 which comprises reacting a compound of formula



with a carboxylic acid of formula HOX , which may be substituted, optionally mixing the product with a compound of formula



emulsifying or dispersing the mixture in water, optionally in the presence of a tertiary amine and polymerising the said isocyanate(s) with a compound of formula $HK - R^{III} - K^IH$. (The polymerisation proceeds by reaction of the $-NCO$ groups).

32 A process as claimed in Claim 30 which comprises reacting the NCO functions of a compound of formula (8) with an excess of a compound of formula $HK R^{III} K^IH$, under mild conditions, such that substantially no reaction with the $N = C = N$ - groups occurs if the desired group X is not a $KR^{III} KH$ group and in that case reacting the product with a compound of formula HX or HOX having the desired group X , reacting the resulting product, optionally together with a compound of formula $HK - R^{II} - KH$, with a diisocyanate of formula $OCN-R-NCO$ and/or $OCN-R^I-NCO$ to produce a product with terminal NCO -functions and polymerising it as a dispersion, optionally in the presence of a tertiary amine in an aqueous medium with a compound of formula $HK (R^{III})_x K^IH$.

33 A process according to any of Claims 30-32 in which an isocyanate capping agent, preferably an alkylamine,

(for example a dialkylamine, an aminoalkanol or a di-(hydroxyalkyl)amine is present.

34 An aqueous dispersion or emulsion of a polymer which is prepared by a process according to any one of Claims 30 to 33.

35 A process of preparing a crosslinked coating by applying an aqueous dispersion of a polymer according to any of Claims 1 to 28 or 34 which comprises C = C bonds together with a photoinitiator onto a surface evaporating the water and subjecting to coated material to UV-radiation.

36 Leather, artificial leather, wood, metal, glass, synthetic material, concrete stone, paper, fabrics, eg woollen fabrics, rubber coated with a polymer according to any preceding claim.

37 Leather treated with a polymer or composition according to any preceding claim which interacts with collagen in the leather in which X contains one or more of the following functional groups: carbonyl groups, electrophilically activated unsaturated groups, halogenated aliphatic or aromatic hydrocarbon groups or phosphonic acid groups.

38 A water-borne functionalised polymer comprising: the addition product of a carbodiimide oligomer and a reactive hydrogen compound HX or HOX, in which X is a polymer modifying group, a chain extender and optionally a polyurethane prepolymer.

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C08G18/08 C08G18/79 C14C11/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C08G C14C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 490 150 (BAYER) 17 June 1992 see page 2, line 39 - page 8, line 57; claims 1-9 ---	1,21,26, 36
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
14 December 1995		29. 12. 95
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016		Authorized officer Bourgonje, A

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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